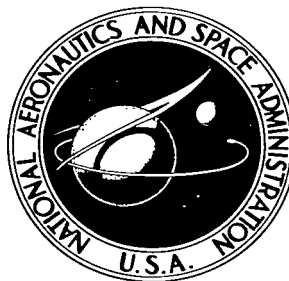


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# PROPOSED MECHANISM FOR THERMOPHOTOTROPIC BEHAVIOR IN PEROVSKITE-STRUCTURED TITANATES

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*Goddard Space Flight Center*  
*Greenbelt, Maryland*



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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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## **SUMMARY**

Many compounds in the solid or liquid state have been known to change color when exposed to electromagnetic radiation. Thermophototropism is the term used to describe the phenomena of radiation-induced coloration and thermally stimulated reversion to the original state. As a result of experimental investigations by the author, a mechanism is proposed to account for thermophototropic behavior in perovskite-structured alkaline-earth titanates. A brief review of these experimental results and of several theories reported in the literature is included.



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## INTRODUCTION

The fundamental optical absorption edges for electronic transitions in the titanates of barium, calcium, and strontium at room temperature occur at about 3950Å, 3650Å, and 3850Å, respectively (References 1-3). Figure 1 illustrates the room temperature spectral reflectance in arbitrary units measured with a spectrophotometer by using pressed powder ceramic titanate samples fired in air. The fundamental absorption of titanium dioxide occurs in the same region of wavelengths (References 4 and 5). Figure 2 is the spectral reflectance of titanium dioxide measured under the same conditions. The photon energies corresponding to the electronic energy gap of these materials lie near the value of  $h\nu$  of the order of 3.3 eV.

It has been shown that when pure ceramic  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$ ,  $\text{CaTiO}_3$ , and  $\text{TiO}_2$  are exposed to ultraviolet radiation at room temperature, no phototropic reaction occurs (References 5-13). When impure (or doped) specimens are irradiated under the same conditions, a noticeable color change ensues. However, irradiation of doped samples at room temperature with filtered light of  $\lambda \geq 5300\text{Å}$  does not induce phototropy. Figures 3-6 are typical results obtained under these conditions. The upper curves represent the spectral reflectance of the bleached specimens. (A bleached sample is one which has been heated to about 250°C in air or vacuum and is white in appearance.) The lower curves represent the reflectance obtained after these samples were irradiated by a mercury light source. It can be seen that the relatively pure material shows slight phototropy due to the residual amounts of impurities present. The reflectance loss in the visible region of the spectrum after irradiation indicates the degree of coloration.

Typical impurities and their concentrations are given in Table 1 for both pure and impure barium titanate. The impurities may enter into the lattice substantially.  $\text{Ti}^{4+}$  can be replaced (References 14-16) by the transition elements (characterized by an incomplete d shell) such as  $\text{Zr}^{4+}$  and  $\text{Nb}^{5+}$ , or by ions of similar size, such as  $\text{Al}^{3+}$ . Other impurities such as  $\text{Sr}^{2+}$  or  $\text{Ca}^{2+}$  can be substituted for  $\text{Ba}^{2+}$  (References 17 and 18).

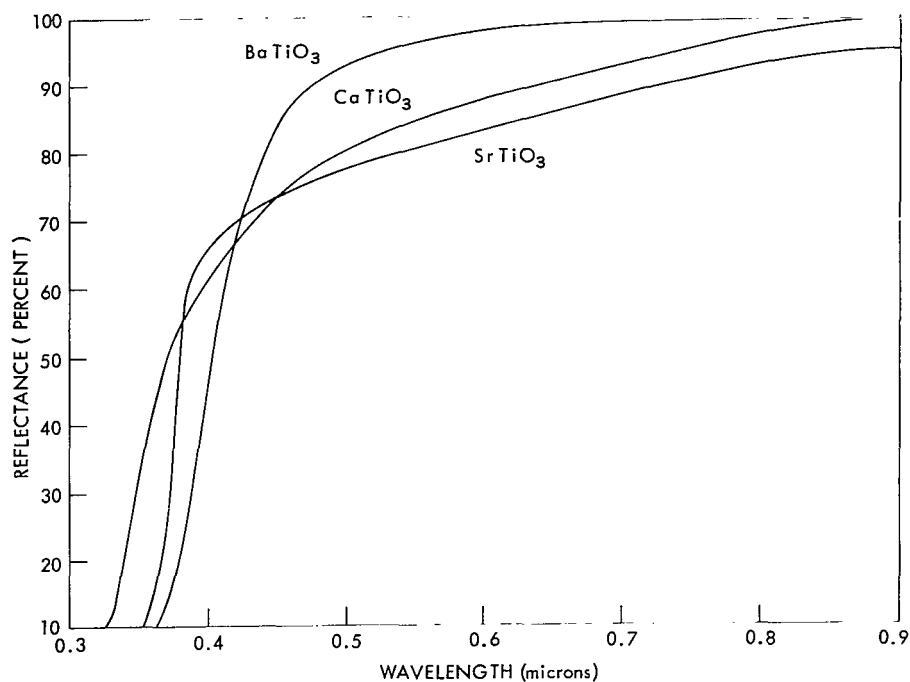


Figure 1—Reflectance as a function of wavelength for BaTiO<sub>3</sub>, CaTiO<sub>3</sub>, and SrTiO<sub>3</sub> in arbitrary units.

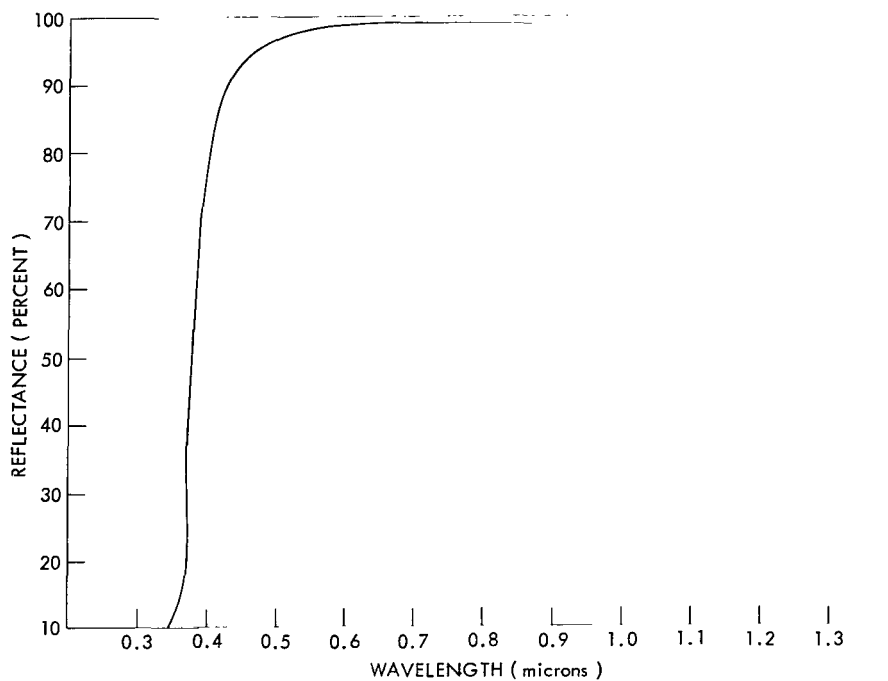


Figure 2—Reflectance as a function of wavelength for TiO<sub>2</sub> in arbitrary units.

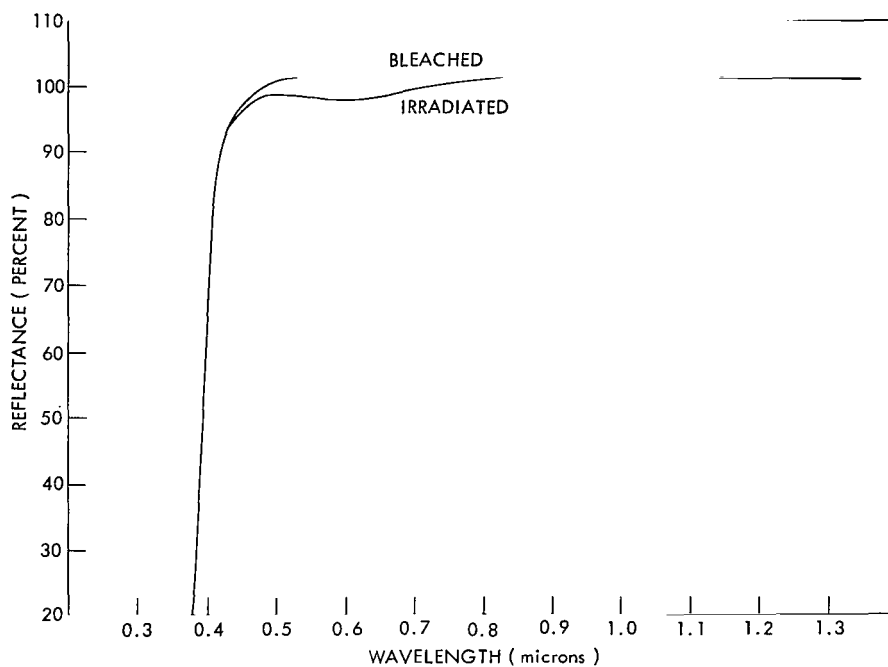


Figure 3—Reflectance as a function of wavelength for bleached and irradiated, chemically pure  $\text{BaTiO}_3$ .

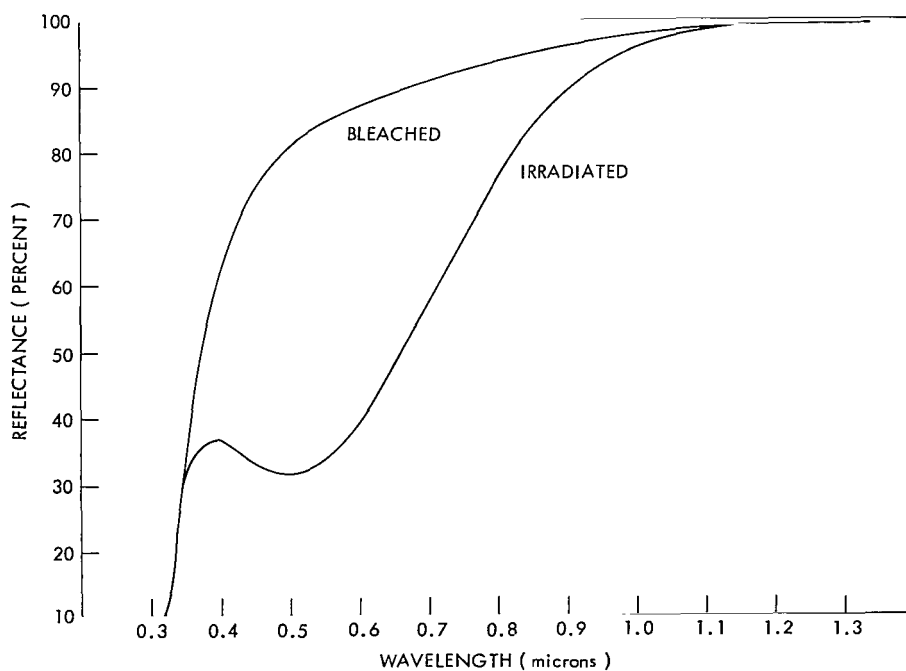


Figure 4—Reflectance as a function of wavelength for bleached and irradiated, relatively impure  $\text{CaTiO}_3$ , in arbitrary units.



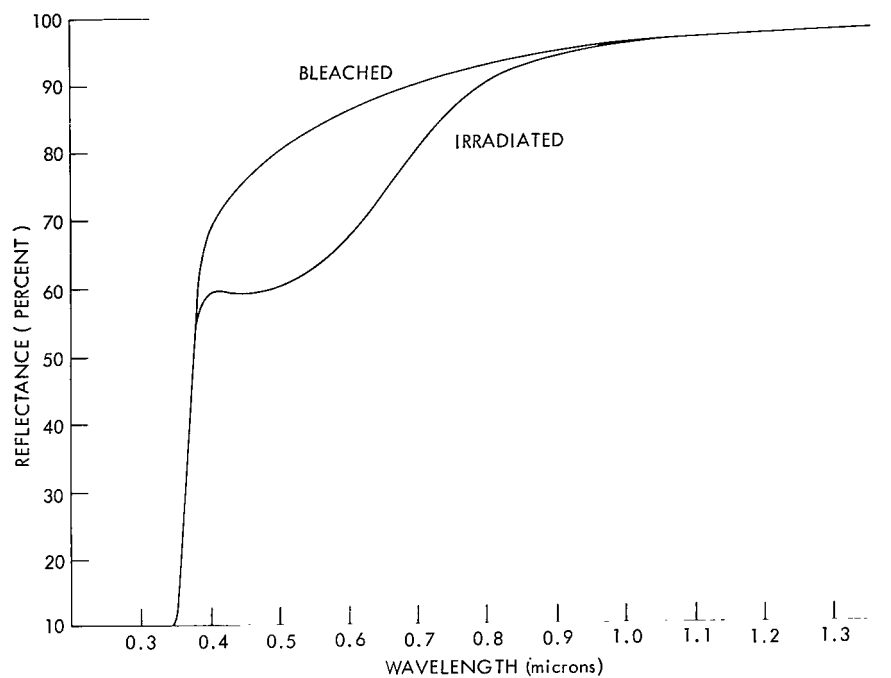


Figure 5—Reflectance as a function of wavelength for bleached and irradiated relatively impure  $\text{SrTiO}_3$ , in arbitrary units.

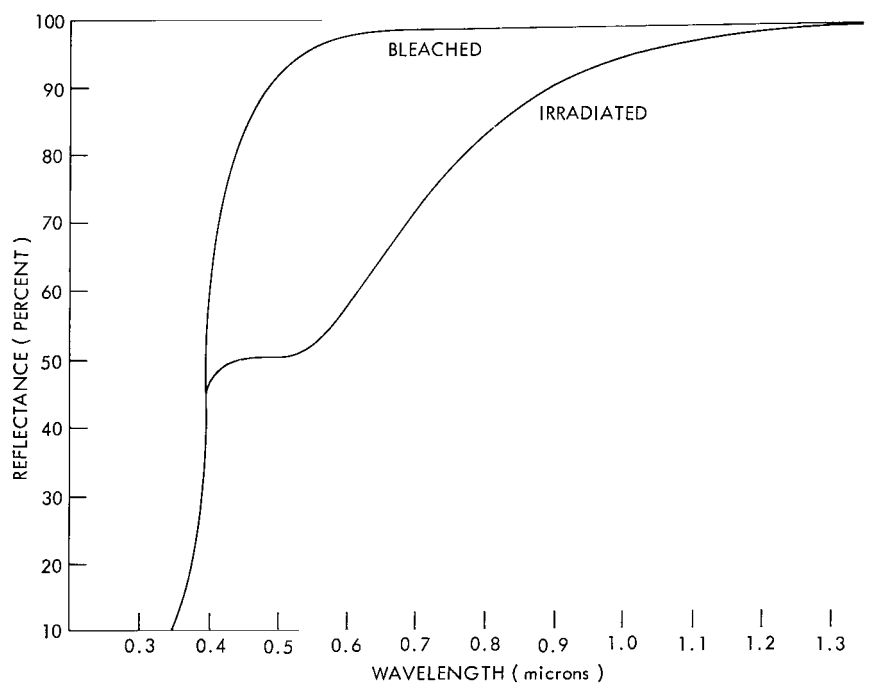


Figure 6—Reflectance as a function of wavelength for bleached and irradiated, relatively impure  $\text{BaTiO}_3$ , in arbitrary units.

## REVIEW OF EXPERIMENTAL RESULTS

The crystalline structures of barium, calcium, and strontium titanate are of the perovskite type, oxygen forming regular octahedra about the titanium ion (Reference 19). These titanates have the formula  $A^{2+} B^{4+}O_3$ , where the quadrivalent cation is surrounded by the octahedra and the divalent cation occupies the large holes between the octahedra. A somewhat similar octahedral structure exists in rutile ( $TiO_2$ ) (References 5 and 20). These compounds exhibit thermophototropic behavior. In contrast, neither pure nor doped magnesium titanate which crystallizes in the cubic close-packed ilmenite structure (Reference 21) changes color upon irradiation (Reference 7). The ilmenite structure does not have the Ti-O chains present in the perovskite form. Although each Ti atom is surrounded by six O atoms, only the oxygens form a close-packed configuration, the Mg and Ti ions being in the interstices.  $CaTiO_3$  has a structure in which Ca and O form a close-packed cubic lattice.

In previous experiments at the Goddard Space Flight Center the behavior of these phototropes have been investigated for various values of temperature, vacuum and gaseous ambients, and selective spectral irradiation. The results are reviewed briefly here. The material is obtained in powdered form die-pressed at about 10,000 psi into disc-shaped pellets, air-fired at 1100°C for about 1 hour and allowed to cool slowly for several hours. The samples are exposed to the radiation of a mercury lamp or carbon arc. Spectroreflectance measurements are made before and after irradiation. The reflectometer range extends from

Table 1

Impurities and Their Concentrations  
(by Weight Percentage).\*

Constituents	Chemically Pure $BaTiO_3$ (lot 302)	$BaTiO_3$ (lot 58C)
$B_2O_3$	<0.005	<0.01
$SiO_2$	0.005	0.45
$P_2O_5$	<0.3	0.17
$ZrO_2$	0.03	0.05
$Sb_2O_3$	<0.01	0.01
$HfO_2$	<0.02	<0.02
$Al_2O_3$	0.03	0.27
$Fe_2O_3$	0.002	0.01
$MnO_2$	<0.0005	0.005
$PbO$	<0.005	<0.005
$MgO$	0.005	0.01
$SnO_2$	<0.005	0.005
$Nb_2O_5$	<0.01	<0.01
$WO_3$	<0.05	<0.05
$Cr_2O_3$	<0.002	<0.002
$NiO$	<0.005	<0.005
$TiO_2$	34.42	33.55
$MoO_3$	<0.01	<0.01
$CaO$	0.03	0.09
$V_2O_5$	<0.003	<0.01
$CuO$	0.0001	0.0005
$ZnO$	<0.2	<0.2
$BaO$	65.35	63.94
$SrO$	0.05	0.42
$Na_2O$	0.005	0.22
$Li_2O$	<0.005	<0.005
$K_2O$	<0.01	0.03
$SO_3$	-	0.21
$CO_2$	-	0.47

\*Material and chemical analysis supplied by the National Lead Company, Titanium Alloy Manufacturing Division, New York City.

0.2 to 2.4 microns.\* The pure and impure samples behave as previously discussed when irradiated in air. After firing or bleaching, a specimen appears white. Following irradiation in air it appears pink-violet or red-brown. At room temperature this darkened state persists after irradiation, essentially unchanged in color. The process of coloration is thermally reversible in that heating the darkened sample will induce a reversion to the original bleached state. The color change saturates after approximately 30 minutes of irradiation and no coloration penetrates below the surface, even after many hours of irradiation. Irradiation with photons of energy appreciably less than that of the band gap will not induce phototropy.

Irradiating an air-bleached sample in a vacuum of the order of  $10^{-5}$  mm of Hg causes a 55 percent reduction in the phototropic response at 5000A compared with that exhibited in air. Irradiating a vacuum-bleached or air-bleached sample in air or oxygen at 1 atm yields a relatively large or the maximum color change (depicted in Figures 4-6). Vacuum heating prior to room temperature vacuum irradiation (with no intermediate exposure to air) almost, if not completely, eliminates the phototropic response. The temperature at which this occurs is greatest for  $\text{CaTiO}_3$ . Irradiating a vacuum-bleached sample in 1 atm of nitrogen at room temperature yields a 60 percent reduction in the phototropic response at 5000A compared with that in air. Under similar conditions in an argon atmosphere the phototropic response at the same wavelength is reduced by 77 percent. (Both  $\text{N}_2$  and Ar contain residual  $\text{O}_2$  gas.) Irradiating a vacuum-bleached sample in oxygen at  $10^{-2}$  mm of Hg (equivalent to a partial pressure of oxygen between that in nitrogen and that in argon at 1 atm) results in a response value intermediate between that for nitrogen and argon (see Table 2).

Specimens irradiated at progressively elevated temperatures either in vacuum or in air exhibit progressively reduced phototropic responses. An upper temperature exists for all the compounds, above which darkening cannot occur. Irradiating a specimen in air at lowered temperatures, down to that of liquid nitrogen, will cause rapid darkening much like that at room temperature. However, the color quickly bleaches out as the sample returns to room temperature. Cooling a darkened sample does not alter its state. Table 2 summarizes these results.

X-ray analysis of  $\text{BaTiO}_3$  at room temperature showed no detectable phase change between the darkened and bleached states. No phosphorescence radiation was detectable from a darkened sample at room temperature

## DISCUSSION OF THE PROPOSED MECHANISM

It is apparent that thermophototropism (TPT) is manifested in the alkaline-earth titanates when three major conditions prevail: (1) a perovskite-type structure exists, oxygen forming octahedral bonds about the titanium atom. The ionic radii of Sr, Ca, and Ba differ considerably (Reference 22), but this is relatively insignificant in regard to the existence of TPT in a

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\*Spectroreflectance data have not been reproduced here beyond 13,500A, since the phototropic reaction does not alter the characteristic reflectivity in the longer wavelength region at room temperature.

Table 2

## Summary of Experimental Results

Experimental Conditions for BaTiO <sub>3</sub> <sup>(a)</sup>	Reflectance R or Change of Reflectance $\Delta R$ at 5000Å
Impure or pure sample fired or bleached in air.	Maximum R
Impure or pure sample bleached in vacuum of $8 \times 10^{-5}$ mm Hg at approximately 180°C.	Maximum R
Impure sample bleached in air, then exposed <sup>(b)</sup> in air at room temperature (r. t.).	$\Delta R \sim -43$ percent <sup>(c) (d)</sup>
Impure sample bleached in air, then exposed in vacuum at r. t.	$\Delta R \sim -19$ percent
Impure sample bleached in vacuum, then exposed in vacuum at r. t.	$\Delta R \sim$ negligible
Impure sample bleached in vacuum, then exposed in 1 atm O <sub>2</sub> or air r. t.	$\Delta R \sim -39$ percent
Impure sample bleached in vacuum, then exposed in 1 atm N <sub>2</sub> at r. t.	$\Delta R \sim -17$ percent
Impure sample bleached in vacuum, then exposed in 1 atm argon at r. t.	$\Delta R \sim -9$ percent
Impure sample bleached in vacuum, then exposed in O <sub>2</sub> at 0.02 mm Hg at r. t.	$\Delta R \sim -12$ percent
Darkened sample bleached in air or vacuum.	$\Delta R \sim +41$ percent <sup>(e)</sup>
Darkened sample left unexposed for several days at r. t.	$\Delta R \sim +1$ percent
Bleached sample exposed to radiation of $\lambda \gtrsim 5200\text{Å}$ .	$\Delta R = 0$
Bleached impure sample exposed to radiation of 3000-4200Å.	$\Delta R \sim -30$ percent <sup>(f)</sup>
Impure sample bleached, then exposed in air at 80°C. <sup>(g)</sup>	$\Delta R \sim -41$ percent
Impure sample bleached, then exposed in air at 140°C. <sup>(g)</sup>	$\Delta R \sim -36$ percent
Impure sample bleached, then exposed in air at 250°C. <sup>(g)</sup>	$\Delta R \sim -24$ percent
Impure sample bleached, then exposed near liquid nitrogen temperature.	$\Delta R \gtrsim -30$ percent
Relatively pure sample bleached, then exposed in air at r. t.	$\Delta R \sim -3$ percent
Relatively pure sample bleached, then exposed in air near liquid N <sub>2</sub> temperature.	$\Delta R \gtrsim -15$ percent

(a) Similar results are true for CaTiO<sub>3</sub> and SrTiO<sub>3</sub>, differing only in degree.

(b) All exposures are for 30 minutes for a low pressure mercury source.

(c) Forty-three percent is about the maximum change found for BaTiO<sub>3</sub> samples with the previously mentioned impurities.

(d) The negative sign means that the initial reflectance  $>$  final reflectance and the sample becomes darkened (colored). Thus in item 3 above  $R_i$  is of the order of 0.93 and  $R_f$  is of the order of 0.50, so that  $\Delta R = R_f - R_i$  is of the order of  $-43$  percent. A positive  $\Delta R$  means that the sample bleached.

(e) Vacuum-bleached samples are sometimes a bit whiter than air-bleached samples. No distinction is made in this report.

(f) The reduced value of  $\Delta R$ , compared with item 3, is due to the lower intensity of irradiation caused by filter attenuation.

(g) Similar results are true for exposures in vacuum at elevated temperatures, differing only in degree.

perovskite-structured environment.\* (2) Appreciable concentrations of certain types of impurities are present, as is readily seen from a comparison of Figures 3 and 4-6. (3) An oxygen-containing gaseous ambient is present. The responses observed from thermal-vacuum studies, together with the different gaseous ambients (and associated oxygen and water vapor content) strongly indicate that TPT is primarily an oxygen-dependent surface phenomenon.

The suggested mechanism is as follows: Ceramic oxides are known to be oxygen deficient (References 5 and 23-25) with a high density of surface vacancies. Further, surface sorption and desorption is readily accomplished (Reference 26). When the material is exposed to an air ambient, oxygen atoms adhere to the surface and form Ti-O bonds. Subsequent ultraviolet irradiation of photon energy approximately equal to or greater than the energy gap photoionizes electrons from the Ti-O bonds. Except for compounds with high concentrations of trivalent impurities, non-stoichiometric material with an excess of titanium behaves as an n-type semiconductor, the impurities acting as trapping centers for the conduction electrons from the Ti-O source at the surface. The impurity levels lie below and close to the conduction band in the forbidden energy gap. The reduction of impurities to less stable valence states causes coloration and a non-discrete or broad-band absorption is exhibited, characteristic of interacting wave functions in solids (Reference 23). Reduction of impurities increases the electrical conductivity appreciably (References 27-30), and increases over several orders of magnitude have been reported with sample darkening (Reference 31). It is likely that the conductivity is essentially electronic in nature (References 27-31)<sup>†</sup> the oxygen ions remaining at the surface in the role of recombination centers. This point will be discussed subsequently in conjunction with thermoluminescent behavior. It follows from the results of thermal-vacuum studies that the source of the migrating charge must lie at the surface. An air-bleached or vacuum-bleached sample irradiated in air has a maximum amount of ionizable surface bonds available and, therefore, exhibits the maximum response. Placing an air-bleached sample in vacuum will desorb a substantial<sup>‡</sup> amount of surface oxygen, with the result that vacuum irradiation yields a reduced phototropic response. Vacuum bleaching will accelerate the surface desorption to the extent that subsequent vacuum irradiation will not produce coloration. The entire process can be represented by an energy band scheme. Depending on the particular divalent cation, the fundamental energy gap of these titanates at room temperature is about 3.3 ev. Since  $\text{TiO}_2$  exhibits the same absorption limit it seems plausible that the gap energy corresponds to the first electronic ionization potential of the Ti-O bond. Except for impurities, trapping mechanisms such as structural defects, including oxygen vacancies, play a relatively insignificant roll in the coloration process itself, at least at or above room temperature. It has been found that abrading the surface reduces the phototropic response by introducing a greater density of surface traps. Bleaching a darkened sample thermally-ionizes the trap levels, causing the electrons to fall back to the valence band predominantly by means of recombination at the surface.

\*A large variation of ionic size will degrade the symmetry, producing non-perovskite structure. This case is excluded from the discussion.

<sup>†</sup>Also see the abstracts by M. Mashkovitch from the All-Union Conference on the Physics of Dielectrics, 1956.

<sup>‡</sup>Strictly speaking, this is true primarily for  $\text{BaTiO}_3$  and  $\text{SrTiO}_3$ . Because of the greater energy gap associated with  $\text{CaTiO}_3$ , the thermophototropic response in vacuum at room temperature is only slightly altered. Thus, as expected, a higher temperature was necessary, in both vacuum and air, to fully bleach  $\text{CaTiO}_3$ . The larger gap energy in  $\text{CaTiO}_3$  is presumably due to the shorter Ti-O bond lengths in the octahedra, the larger force constants yielding stronger electronic bonds.

From this model it follows that radiative electronic transitions must occur and recombination radiation should be observed. Coloration produced at room temperature remains relatively stable as long as the sample remains at that temperature. It is only during a rapid bleaching process that recombination radiation can be detected.

Theoretically no low temperature bound for phototropic activity is expected. Thus samples were darkened at liquid nitrogen temperatures and bleached by being allowed to return rapidly to room temperature. During this process thermoluminescence was observed, corresponding to the emptying of shallow trapping levels. These shallow energy levels are effective at low temperatures only and cause darkening comparable with that at room temperature. Further, relatively pure  $\text{BaTiO}_3$  samples were exposed at liquid nitrogen temperatures and the darkening was considerably greater than for exposure at room temperature. However, the change was only about half that found in relatively impure  $\text{BaTiO}_3$  at low temperature.

These results tend to indicate that the thermophototropic response is strongly influenced by the type and concentration of traps. Increasing the type and concentration of impurities having trap energies effective at room temperature will produce a greater color change at that temperature. Similarly, bleaching temperatures may be lowered by excluding impurities with deeply lying energy states. Experiments with gaseous ambients did indicate, as expected, a strong correlation between TPT and the presence of oxygen. It is likely that the oxygen ions remain at the surface after ionization radiation darkens the specimen. The presence of these ions maintains the electrical neutrality of the crystal and these ions are the recombination centers for thermoluminescent behavior.

## CURRENT THEORIES

Several qualitative theories of TPT in the compounds discussed have appeared in the literature. MacNevin and Ogle conclude that it is structure-dependent, because of the nonresponsive nature of  $\text{MgTiO}_3$  (Reference 7). Further, the presence of certain specific impurities is essential, those having valences other than +4 are needed for electron transfer to occur and ionic radii near that of  $\text{Ti}^{4+}$  are necessary to fit the lattice with only moderate distortion. MacNevin and Ogle also found that phototropic response increased with impurity concentration but that neither moisture nor oxygen influenced the color change. They attributed some of the darkening in  $\text{CaTiO}_3$  to the reduction of  $\text{Ti}^{4+}$  to colored  $\text{Ti}^{3+}$ . Since there was no mention of preoxidation heating and since the alkaline-earth titanates do not accept more oxygen than the stoichiometric composition calls for (Reference 28) it is readily understood why the oxygen dependence was not found.

Kosman and Bursian attribute the darkening of polycrystalline  $\text{BaTiO}_3$  to the partial reduction and precipitation of the metal (Reference 29). However, they do not consider the role of impurities nor surface ambients.

Tanaka (Reference 8) reported surface coloration in  $\text{CaTiO}_3$ , due to daylight, x-ray, and ultraviolet radiation, which did not fade in the dark, was dependent on the presence of impurities,

and was thermoreversible. He inferred that TPT is moisture dependent since it did not occur in the presence of phosphorous pentoxide. He concluded that some impurity decomposes water photochemically, and that the hydrogen formed thereby acts to reduce  $\text{TiO}_2$  to a lower oxide, causing color. It is difficult to reconcile Tanaka's theory with the fact that increased concentrations of oxygen increase the color change.

Weyl and his co-workers (References 32-34) conclude that when light strikes an impurity ion, say  $\text{Fe}^{3+}$ , an electron of the foreign ion is excited. It moves either into an oxygen vacancy of the defective structure, thereby producing  $\text{Fe}^{4+}$ , or attaches itself to a  $\text{Ti}^{4+}$  ion to give colored  $\text{Ti}^{3+}$ . This mechanism cannot be entirely accepted since it permits coloration independent of an ambient. Further, different impurities having different activation energies will negate the critical dependence of TPT on wavelength.

Bear and McTaggart (References 4 and 6), working with various mixtures of anatase and rutile and a number of other host oxides, conclude that impurities are adsorbed at the surface or at interfaces. They found that samples sealed in vacuum with moisture did not develop color when irradiated; thus an oxygen-containing atmosphere was necessary. The valence state of the impurities is changed by the oxygen when the sample is exposed to light. The valence state of the impurity atoms corresponding to the exposed or unexposed state was not determined conclusively. They believe that the impurity is oxidized by light causing the sample to darken, that the reduced form of the impurity is the stable form, and that heating reduces the impurity causing bleaching. This is contrary to the valence state found in iron-doped samples by Sellwood and his co-workers (Reference 35). The reversion of valence is accelerated by heating at relatively low temperatures, causing a rapid reversal of color. They feel that the presence of water molecules catalyzes or promotes the development of color by action with oxygen or by entering into the bonding between the impurity and the host oxide. The host oxide converts the incident light energy into a form that activates the valence change of the impurity. Further, they find that the bleaching temperature is strongly dependent on the particular doping substance (iron-doped oxides bleach at  $100^\circ\text{C}$ , chromium-doped oxides at  $190^\circ\text{C}$ , and vanadium-doped oxides at about  $175^\circ\text{C}$ ). Although they do not specify how light energy activates a valence change, nor the exact roles played by oxygen and water molecules, their conclusions generally coincide with those presented here for the perovskite titanates.

## CONCLUSION

A mechanism has been proposed which accounts for thermophototropic behavior in  $\text{BaTiO}_3$  and related material. A high density of surface vacancies results in oxygen adsorption. Radiation with photon energies approximately equal to or greater than the gap energy frees electrons from the Ti-O bonds formed at the surface. The conduction electrons reduce the impurities present in the material causing coloration. Reversion to the original color is achieved by thermal ionization of the impurity levels accompanied by recombination radiation.

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## REFERENCES

1. Horie, T., Kawabe, K., and Sawada, S., "Optical Behaviour of Multi-Domain Single Crystal of  $\text{BaTiO}_3$  in Dependence on Temperature," *Phys. Soc. Japan J.* 9(5):823-825, September-October 1954.
2. Linz, A., and Herrington, K., "Electrical and Optical Properties of Synthetic Calcium Titanate Crystal," *J. Chem. Phys.* 28(5):824-825, May 1958.
3. Noland, J. A., "Optical Absorption of Single-Crystal Strontium Titanate," *Phys. Rev.* 94:724, May 1, 1954.
4. Bear, J., and McTaggart, F. K., "Phototropic Effects in Oxides. II. White Oxides in General," *J. Appl. Chem.* 8(1):72-76, 1958.
5. Breckenridge, R. G., and Hosler, W. R., "Electrical Properties of Titanium Dioxide Semiconductors," *Phys. Rev.* 91:793-802, August 15, 1953.
6. McTaggart, F. K., and Bear, J., "Phototropic Effects in Oxides. I. Titanium Dioxide," *J. Appl. Chem.* 5:643-653, 1955.
7. MacNevin, W. M., and Ogle, P. R., "Phototropy of the Alkaline Earth Titanates," *Amer. Chem. Soc. J.* 76:3846-3848, 1954.
8. Tanaka, Y., "Studies on the Reactions between Oxides in Solid State at Higher Temperatures. II. The Reaction between Calcium Oxide and Titanium Oxide and the Photo-Sensitivity of Calcium Titanate," *Chem. Soc. Japan Bull.* 16(12):455-463, December 1941.
9. Levin, S. B., Field, N. J., Plock, F. M., and Merker, L., "Some Optical Properties of Strontium Titanate Crystal," *Opt. Soc. Amer. J.* 45(9):737-739, September 1955.
10. Williamson, W. O., "Darkening of Some Commercial Titanium Dioxide in Daylight," *Nature* 140:238-239, 1937.
11. Williamson, W. O., "Photosensitive Titanium Dioxide," *Nature* 143:279, 1939.
12. Williamson, W. O., "Reversible Photosensitivity in Some Artificial Materials Containing Rutile," *Mineralog. Mag.* 25:513-528, 1940.



13. Williamson, W. O., "Reversible Darkening in Daylight of Some Glazes Containing Titanium," *Brit. Ceram. Soc. Trans.* 39:345-365, 1940.
14. McQuarrie, M., and Behnke, F. W., "Structural and Dielectric Studies in the System (Ba, Ca)-(Ti, Zr)-O<sub>3</sub>," *Amer. Ceram. Soc. J.* 37:539-543, 1954.
15. Coffeen, W. W., "Dielectric Bodies in Metal Stannate-Barium Titanate Binary Systems," *Amer. Ceram. Soc. J.* 37(10):480-489, October 1, 1954.
16. Wainer, E., and Wentworth, C., "Niobate and Tantalate Dielectrics," *Amer. Ceram. Soc. J.* 35:207-214, 1952.
17. Jonker, G. H., "Keramische materialen voor de electrotechniek," *Chem. Weekblad* 49:932-936, December 5, 1953.
18. Megaw, H. D., "Crystal Structure of Double Oxides of the Perovskite Type," *Phys. Soc. Proc.* 58:133-152, March 1946.
19. Kay, H. F., and Bailey, P. C., "Structure and Properties of CaTiO<sub>3</sub>," *Acta Crystallog.* 10(3):219-226, March 10, 1957.
20. Wyckoff, R. W. G., "Crystal Structures," New York: Interscience Publishers, 1948.
21. Wells, A. F., "Structural Inorganic Chemistry," Oxford, England: The Clarendon Press, 1945.
22. Rankama, K., and Sahama, T. G., "Geochemistry," Chicago: University of Chicago Press, 1950.
23. Kingery, W. D., "Introduction to Ceramics," New York: John Wiley, 1960.
24. Anliker, M., Brugger, H. R., and Känzig, W., "Das Verhalten von kolloidalen Seignetteelektrika III, Bariumtitanat BaTiO<sub>3</sub>," *Helv. Phys. Acta* 27(2):99-124, 1954.
25. Känzig, W., "Space Charge Layer Near the Surface of a Ferroelectric," *Phys. Rev.* 98(2):549-550, April 15, 1955.
26. Adamson, A. W., "Physical Chemistry of Surfaces," New York: Interscience Publishers, 1960.
27. Cronmeyer, D. C., "Electrical and Optical Properties of Rutile Single Crystals," *Phys. Rev.* 87:876-886, September 1, 1952.
28. Weise, E. K., and Lesk, I. A., "On The Electrical Conductivity of Some Alkaline Earth Titanates," *J. Chem. Phys.* 21:801-806, May 1953.
29. Kosman, M. S., and Bursian, E. V., "Coloration of BaTiO<sub>3</sub> Crystals," *Dokl. Akad. Nauk SSSR* 115(3):483-485, 1957 (In Russian).

30. Salmang, H., "Ceramics: Physical and Chemical Fundamentals," (Translated by M. Francis) London: Butterworths Publications, 1961.
31. Novosiltsev, N. S., Khodakov, A. L., and Shulman, M. C., "Metastabilnie sostoyaniya BaTiO<sub>3</sub>," *Dokl. Akad. Nauk SSSR* 83(6):829-831, April 1952.
32. Weyl, W. A., and Förland, T., "Photochemistry of Rutile," *Indus. Eng. Chem.* 42:257-263, 1950.
33. Johnson, G., and Weyl, W. A., "Influence of Minor Additions on Color and Electrical Properties of Rutile," *Amer. Ceram. Soc. J.* 32(12):398-401, December 1, 1949.
34. Weyl, W. A., and Terhune, N., "Crystal Chemistry Applied to Foreign Atoms in Titanate Ceramics," *Ceram. Age* 61:22, August 1953.
35. Selwood, P. W., Ellis, M., and Wethington, K., "Supported Oxides of Iron," *Amer. Chem. Soc. J.* 71:2181-2184, 1949.